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(54) METHOD AND APPARATUS FOR MULTIVARIATE CHARACTERIZATION OF OPTICAL INSTRUMENT RESPONSE

METHODE UND APPARAT ZUR MULTIVARIABLEN CHARAKTERISATION DER ANTWORT EINES OPTISCHEN INSTRUMENTS

PROCEDE ET APPAREIL DE DETERMINATION DES CARACTERISTIQUES A PLUSIEURS VARIABLES DE REPOSE D'APPAREIL OPTIQUE

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US-A- 4 241 997 **US-A- 4 721 657**

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Description

This invention relates, generally, to optical instruments such as spectrometers and, more particularly, to a method and apparatus for calibrating such instruments.

Optical instruments such as spectrometers use light to perform various spectral analyses. Typically, a light beam, after being filtered by a monochromator, interferometer and Fourier transform, scanning filter photometer or the like is directed on an unknown sample to generate a resulting spectrum. The resulting spectrum can then be compared with a known spectrum to determine various characteristics of the unknown sample such as its chemical composition.

As is known in the art, it is critical that any deviations in wavelength and/or the instrument's response to light intensity be accounted for to yield accurate analytical results. If these deviations are not accounted for, the generated spectra will not be representative of the sample but will be attributable, at least in part, to these deviations. As a result, the response of the instrument will be mischaracterized and its performance will be flawed.

Various methods of recalibrating optical instruments have been developed in an attempt to account for deviations in wavelength and response to light intensity. One such recalibration method uses calibration standards or etalon that are representative of the population of unknown samples. For example, if wheat samples are to be analyzed for protein content, the calibration standards or etalon would be a set of wheat samples with known protein contents. When recalibration of the optical instrument is necessary, one or more of the known samples are reanalyzed and the resulting spectra are compared to the standard or etalon spectra from the known samples. The instrument response is then recharacterized such that the spectra from the reanalyzed standard or etalon match the original spectra for the standards or etalon samples.

One problem with such a recalibration method is that the set of calibration standards or etalon for example, the wheat samples with known protein contents) can change and degrade over time. As a result the sample effect will be confounded with the instrument effect such that the spectrum generated will not accurately reflect the instrument response. To avoid using degrade samples, it is possible to reanalyze the standards or etalon or prepare new standards or etalon each time the instrument is recalibrated. These approaches, however, are time consuming and introduce operator variability in reanalyzing or preparing the samples.

An alternative to the recalibration method using representative samples from the population, is to use a so-called etalon as the known sample. Generally, a so-called etalon consists of two parallel surfaces where both surfaces have partial reflection and partial transmission of light. For example, a solid block of germanium in air or two spaced, parallel silver plates are etalons.

The only requirement is that the instrument must respond to the etalon in a way that allows for recalibration.

Examples of laser systems that utilize etalons or standards to recalibrate instrument response can be found in U.S. Patent No. 4,241,997 (Chraplyvy) and "Wavenumber Calibration Of Tunable Diode Lasers Using Etalons", *Applied Optics*, Vol. 17, No. 6, March 15, 1978. These systems, however, disclose the use of an etalon or standard only to recalibrate wavelength and do not address the problem of recalibrating other spectral features such as light intensity. Moreover, to use these recalibration systems, the sample must be removed. In many applications removing the sample is difficult and time consuming.

Thus, an improved method and apparatus for recalibrating optical instruments is desired.

The recalibration method and apparatus of the invention overcomes the shortcomings of the prior art by providing a system in which instrument characteristics such as light intensity can be recalibrated. The applicants have discovered the desirability and feasibility of simultaneously recalibrating an optical instrument's intensity response and wavelength position using an etalon or standard and have developed a method for recalibrating the instrument without removing the sample from the work situs. Moreover, it has been discovered that the use of multiple etalons or standards acting over a single region for recalibration provides improved accuracy. The system consists of a light source, a means of wavelength selection such a monochromator, one or more etalons or other stable samples or standards, a detector and a processor for generating spectra and changing the instrument response. A transfer function can be used to recharacterize the instrument's response to match the actual spectrum with the standard spectrum. Where the sample is not removed from the work situs, the etalon or standard is placed in series with the unknown sample such that a combined spectrum of the sample and etalon or standard is created. The spectrum of the sample alone is then mathematically extracted from the combined spectrum to provide the actual spectrum of the etalon or standard alone. The actual spectrum can then be compared to the standard spectrum and the instrument response recharacterized accordingly.

Figure 1 shows a schematic view of one embodiment of the recalibration system of the invention.

Figures 2A-2D are graphs of the spectra produced using the invention.

Figures 3A and 3B show one example of the recalibration system used in an in situ application.

Figures 4A and 4B are graphs of the spectra illustrating the use of the system in situ.

Referring more particularly to Figure 1, the recalibration system of the invention typically includes a light source 2, a monochromator 4 or other device for generating specific wavelengths, a support 6 for moving one or more standards or etalon into the light path, and a

detector 8. In the preferred embodiment, a plurality of standards or etalon would be used to obtain a more accurate transfer function. The standard 7 although preferably a so-called etalon, can also consist of neutral density filters, polymer standards such as polystyrene or any other stable standard such as glass. It is required only that the etalon or standard 7 provide an instrument response that allows for instrument recalibration for the characteristic of interest. For example, if a particular intensity level of light for a particular wavelength is being analyzed, that wavelength must be within the spectral range of the etalon or standard.

The spectrum is represented on a display, for example computer 10, where a transfer function can be used to recharacterize the instrument response as will hereinafter be described. Reference spectra of the standards or etalon are stored in the computer 10. The reference spectra are generated using an equivalent standard or etalon to the standard or etalon which is to be used for recalibration. As used herein, "equivalent" means either the identical standard or etalon or a virtually identical standard or etalon in effect or function. The reference spectra may be generated by intercepting the light path with the standard or etalon alone or with the standard or etalon in series with a sample, as will be described in greater detail below. The reference spectra are used to characterize the instrument response at time of initial calibration. The computer 10 can also be used to control the position of etalon or standard 7, as will hereinafter be described. Moreover, transfer optics 12 can be used if so desired.

It is contemplated that the recalibration method of the invention can be used with the sample 9 in series with the standard or etalon as shown in Figure 1 or the sample can be removed from the light path prior to recalibration as represented by arrow A. Whether or not the sample 9 and standard or etalon 7 are in series is dictated by the configuration of the system being recalibrated. When the sample 9 and standard or etalon 7 are used in series, the standard spectrum must be mathematically extracted as will be hereinafter explained with reference to Figures 3 and 4. Alternatively, the standard or etalon 7 can be located before the monochromator 4 in the position shown by phantom line 11.

As an example of one use of the above-described system for re-calibration, polystyrene was run under two instrument conditions. Figure 2A is a plot of the resulting spectrum of polystyrene acquired with the voltage to the source at 15.06 volts (solid lined spectra) and a spectrum acquired with the source voltage reduced to 14.625 (dashed line spectra). The voltage to the source was changed from 15.06 to 14.625 to simulate the type of change that can occur in the instrument. For illustrating purposes, the spectrum acquired at 15.06 volts is assumed to be the reference spectrum and would be stored in computer 10. As Figure 2A indicates, the change in source voltage resulted in reduced energy throughput and a baseline offset in the resulting poly-

styrene spectrum. Figure 2B is an expanded view of the region between 1100 and 1660 for the polystyrene spectrum shown in Figure 2A.

A zinc selenide etalon on a quartz substrate was selected as the stable etalon or standard and was also analyzed at both source voltages and a simple spectral difference was used to estimate the instrument change. The resulting transfer function is shown in Figure 2C. The transfer function can be obtained by any suitable mathematical approach such as using linear or nonlinear regression techniques to transform the wavelength and intensity axes, as will be appreciated by one skilled in the art. Using this transfer function, the polystyrene spectra acquired at 14.625 volts were modified to reflect the instrument change from the original spectra acquired at 15.06 volts.

Figure 2D shows the recalibrated spectrum acquired at 14.625 volts plotted with the polystyrene spectrum acquired with the source voltage at 15.06 volts. Because of the recalibration technique, the recalibrated spectrum at 14.625 volts overlies the spectrum at 15.06 volts such that only a single line is visible. Comparing Figure 2A with Figure 2D demonstrates the effectiveness of using the etalon for instrument recalibration as the differences between the re-calibrated spectrum and the original spectrum is negligible.

The applicants have discovered that this calibration method can be used to recharacterize instrument response for light intensity as well as for wavelength. As will be appreciated, this is only one example of the recalibration method of the invention. More stable etalons and/or the use of multiple standards coupled with more sophisticated mathematical methods for deriving the transfer function should yield improved results.

Figures 3A and 3B show schematically the in situ recalibration system where the standard or etalon is in series with the sample being analyzed. For illustrative purposes the recalibration system is shown in conjunction with a chemical reactor 14 having a bath of chemicals 16 being mixed therein. Specifically, the light source fiber optic cable 20, reflector 22 and detector fiber optic cable 26 are housed in a protective sheath 27 submerged in bath 16. Sheath 27 is provided with an aperture 29 defined by windows 31 and 33 into which the bath can enter so as to create a sample between the light source and detector. The light source 2 from a spectrometer projects a light beam through the portion of bath 16 in aperture 29 via fiber optic cable 20. The light projected from cable 20 passes through bath 16, reflects from reflector 22 and is received by detector 8 via fiber optic cable 26. The resulting spectrum received by detector 8 is displayed on processor 10 which also controls the recharacterization of the spectrometer. This system allows the composition of the chemicals being mixed in the reactor 14 to be continuously monitored. While the illustrated embodiment includes a reflector, it will be appreciated that the reflector could be omitted and the detector fiber optic cable be placed in-line with

the light source.

Periodically it is necessary to recalibrate the system. To do so, an etalon or other stable standard 7 is moved between the light source 2 and reflector 22. More preferably, the etalon standard 7 can be moved between the light source 2 and the detector 8 as shown in Figure 3A. Preferably, the etalon or standard 7 can be moved into and out of the path of the light beam by any suitable automated transfer device controlled by computer 10. When the etalon is so positioned, the spectrum generated by detector 8 represents the combined effects of the etalon 30 and/or 7 and the composition of bath 16 as shown by the dotted line in Figure 4A. To find the spectrum for the standard alone, the spectrum of the sample alone (solid line in Figure 4A) is mathematically extracted from the spectrum of the sample and etalon. The extracted spectrum as shown by the dotted line in Figure 4B is compared to the reference spectrum of the standard (solid line in Figure 4B) and transfer equation is used to recalibrate the optical instrument such that the extracted standard or etalon spectrum matches the reference standard spectrum as has previously been described. While one particular application of the invention has been described, it will be appreciated that the system can be used in any application which uses an optical monitoring instrument.

An additional application of the invention is to use etalons or standards to calibrate the response of a plurality of instruments. This application is particularly useful in calibrating process instruments (that is instruments used at on site processes) to respond in the same manner as a lab instrument.

In this application, calibration equations are derived on the lab instrument using a set of known samples. These equations are used to estimate analytical results (for example protein content in wheat) from acquired spectra. Additionally, spectra for plurality of etalons are acquired on the lab instrument to characterize that instrument's response. The etalon spectra are then acquired on each of the process instruments to be calibrated and a transfer function is developed for each process instrument. The transfer function for each process instrument is used on subsequent spectra acquired on that instrument to make the response substantially equivalent to that which would be produced by the lab instrument. Alternatively, the transfer function can be used to modify the calibration equations used to derive analytical results from the acquired spectra rather than modifying the spectra themselves.

While the invention has been described in particular detail with respect to the Figures, it is to be understood that the foregoing description is offered merely by way of example and that the invention is to be limited only by the appended claims.

Claims

1. An optical instrument which generates a variable response that can be calibrated in situ comprising:

- means (2) for generating a light beam,
- means for exposing a sample (9) to the light beam so that a sample spectrum can be generated,
- means (8) for detecting spectra,
- means (10) for storing spectra,

characterized in that it further comprises:

- means (6) for periodically exposing a standard (7) to the light beam so that a current standard spectrum can be generated,
- means (10) for comparing the current standard spectrum to a previously generated standard spectrum stored in the means for storing spectra and for adjusting the instrument response to match the current standard spectrum to the previously generated standard spectrum.

2. The optical instrument of claim 1 wherein a transfer function is used to adjust the instrument response to match the current standard spectrum to the previously generated spectrum.

3. The optical instrument of claims 1 or 2 wherein the means (6) for periodically exposing a standard (7) to the light beam is arranged in series with the means for exposing the sample (9) to the light beam, so that a combined spectrum can be generated and wherein the instrument further comprises a means for extracting the standard spectrum from the combined spectrum.

4. A method for recalibrating an optical instrument of the type having a light source (2) and a light detector (8) for generating a response in the form of a spectrum characteristic of a sample comprising the steps of:

- a) placing a sample (9) between the light source (2) and detector (8),
- b) generating a spectrum corresponding to the sample,

characterized in that it further comprises the steps of:

- c) placing a standard (7) between the light source (2) and detector (8) and in series with the sample,
- d) generating a combined spectrum of the standard and the sample,
- e) extracting the spectrum for the sample from

the combined spectrum for the standard and sample to give a resulting spectrum of the standard and

f) comparing the resulting spectrum of the standard to a reference spectrum and varying the instrument response so that the resulting spectrum matches the reference spectrum.

5. The method according to claim 4 wherein a transfer function is used to vary the instrument response.
6. The method of claim 4 further comprising repeating steps c) through f) for a plurality of standards.
7. The method of any of claims 4 to 6 according to which the reference spectrum is obtained by inserting a standard equivalent to the standard of step c) between the light source (2) and detector (8).

Patentansprüche

1. Optisches Instrument, welches eine variable Antwort erzeugt, die in situ kalibriert werden kann, umfassend:

- ein Mittel (2) zum Erzeugen eines Lichtstrahls,
- ein Mittel, um eine Probe (9) dem Lichtstrahl auszusetzen, so daß ein Probenspektrum erzeugt werden kann,
- ein Mittel (8) zum Erfassen von Spektren,
- ein Mittel (10) zum Speichern von Spektren,

dadurch gekennzeichnet, daß es ferner umfaßt:

- ein Mittel (6), um einen Standard (7) periodisch dem Lichtstrahl auszusetzen, so daß ein momentanes Standardspektrum erzeugt werden kann,
- ein Mittel (10) zum Vergleichen des momentanen Standardspektrums mit einem vorher erzeugten Standardspektrum, welches in dem Mittel zum Speichern von Spektren gespeichert ist, und zum Einstellen der Instrumentenantwort, um das momentane Standardspektrum in Übereinstimmung mit dem vorher erzeugten Standardspektrum zu bringen.

2. Optisches Instrument nach Anspruch 1, worin eine Transferfunktion zum Einstellen der Instrumentenantwort verwendet wird, um das momentane Standardspektrum in Übereinstimmung mit dem vorher erzeugten Spektrum zu bringen.

3. Optisches Instrument nach Anspruch 1 oder 2, worin das Mittel (6) zum periodischen Aussetzen eines Standards (7) dem Lichtstrahl in Reihe mit dem Mittel zum Aussetzen der Probe (9) dem Lichtstrahl an-

geordnet ist, so daß ein kombiniertes Spektrum erzeugt werden kann, und worin das Instrument ferner ein Mittel zum Extrahieren des Standardspektrums aus dem kombinierten Spektrum umfaßt.

4. Verfahren zum Rekalibrieren eines optischen Instruments des Typs, welcher eine Lichtquelle (2) und einen Lichtdetektor (8) zum Erzeugen einer Antwort in der Form eines für eine Probe charakteristischen Spektrums aufweist, umfassend die Schritte:

- a) Anordnen einer Probe (9) zwischen der Lichtquelle (2) und dem Detektor (8),
- b) Erzeugen eines der Probe entsprechenden Spektrums,

dadurch gekennzeichnet, daß es ferner die Schritte umfaßt:

- c) Anordnen eines Standards (7) zwischen der Lichtquelle (2) und dem Detektor (8) und in Reihe mit der Probe,
- d) Erzeugen eines kombinierten Spektrums des Standards und der Probe,
- e) Extrahieren des Spektrums für die Probe aus dem kombinierten Spektrum für den Standard und die Probe, um ein resultierendes Spektrum des Standards zu erhalten, und
- f) Vergleichen des resultierenden Spektrums des Standards mit einem Referenzspektrum und Verändern der Instrumentenantwort derart, daß das resultierende Spektrum mit dem Referenzspektrum übereinstimmt.

5. Verfahren nach Anspruch 4, worin eine Transferfunktion zum Verändern der Instrumentenantwort verwendet wird.
6. Verfahren nach Anspruch 4, ferner umfassend das Wiederholen der Schritte c) bis f) für eine Mehrzahl von Standards.
7. Verfahren nach einem der Ansprüche 4 bis 5, bei welchem das Referenzspektrum durch Einführen eines zu dem Standard des Schritts c) äquivalenten Standards zwischen die Lichtquelle (2) und den Detektor (8) erhalten wird.

Revendications

1. Instrument optique qui produit une réponse variable et qui peut être étalonné sur place, comprenant :
 - un moyen (2) destiné à émettre un faisceau de lumière,
 - un moyen destiné à exposer un échantillon (9)

- au faisceau de lumière de manière à pouvoir produire un spectre d'échantillon,
- un moyen (8) destiné à détecter les spectres,
 - un moyen (10) destiné à conserver les spectres,

caractérisé en ce qu'il comprend en outre :

- un moyen (6) destiné à l'exposition périodique d'un étalon (7) au faisceau de lumière de manière à produire un spectre courant d'étalon,
 - un moyen (10) destiné à comparer le spectre courant d'étalon à un spectre d'étalon précédemment produit et conservé dans le moyen destiné à conserver les spectres, et à régler la réponse de l'instrument de façon que le spectre courant d'étalon concorde avec le spectre d'étalon précédemment produit.
2. Instrument optique selon la revendication 1, dans lequel on utilise une fonction de transfert pour régler la réponse de l'instrument de façon que le spectre courant d'étalon concorde avec le spectre d'étalon précédemment produit.
3. Instrument optique selon l'une des revendications 1 ou 2, dans lequel le moyen (6) destiné à l'exposition périodique d'un étalon (7) au faisceau de lumière est monté en série avec le moyen destiné à exposer l'échantillon (9) au faisceau de lumière, de manière à pouvoir produire un spectre combiné, l'instrument comprenant en outre un moyen destiné à extraire le spectre d'étalon du spectre combiné.
4. Procédé de réétalonnage d'un instrument optique du type comportant une source de lumière (2) et un photodétecteur (8) pour produire une réponse sous la forme d'un spectre caractéristique d'un échantillon, comprenant les étapes de :
- a) mise en place d'un échantillon (9) entre la source de lumière (2) et le détecteur (8);
 - b) production d'un spectre correspondant à l'échantillon,
- caractérisé en ce qu'il comprend en outre les étapes de :
- (c) mise en place d'un étalon (7) entre la source de lumière (2) et le détecteur (8) et en série avec l'échantillon,
 - d) production d'un spectre combiné de l'étalon et de l'échantillon,
 - e) extraction du spectre concernant l'échantillon du spectre combiné pour l'étalon et l'échantillon, afin de donner un spectre résultant de l'étalon, et
 - f) comparaison du spectre résultant de l'étalon

à un spectre de référence, et modification de la réponse de l'instrument de façon que le spectre résultant concorde avec le spectre de référence.

- 5. Procédé selon la revendication 4, dans lequel on utilise une fonction de transfert pour modifier la réponse de l'instrument.
- 6. Procédé selon la revendication 4, comprenant en outre la répétition des étapes c) à f) pour une pluralité d'étalons.
- 7. Procédé selon l'une quelconque des revendications 4 à 6, selon lequel on obtient le spectre de référence en intercalant, entre la source de lumière (2) et le détecteur (8), un étalon équivalent à l'étalon de l'étape c).

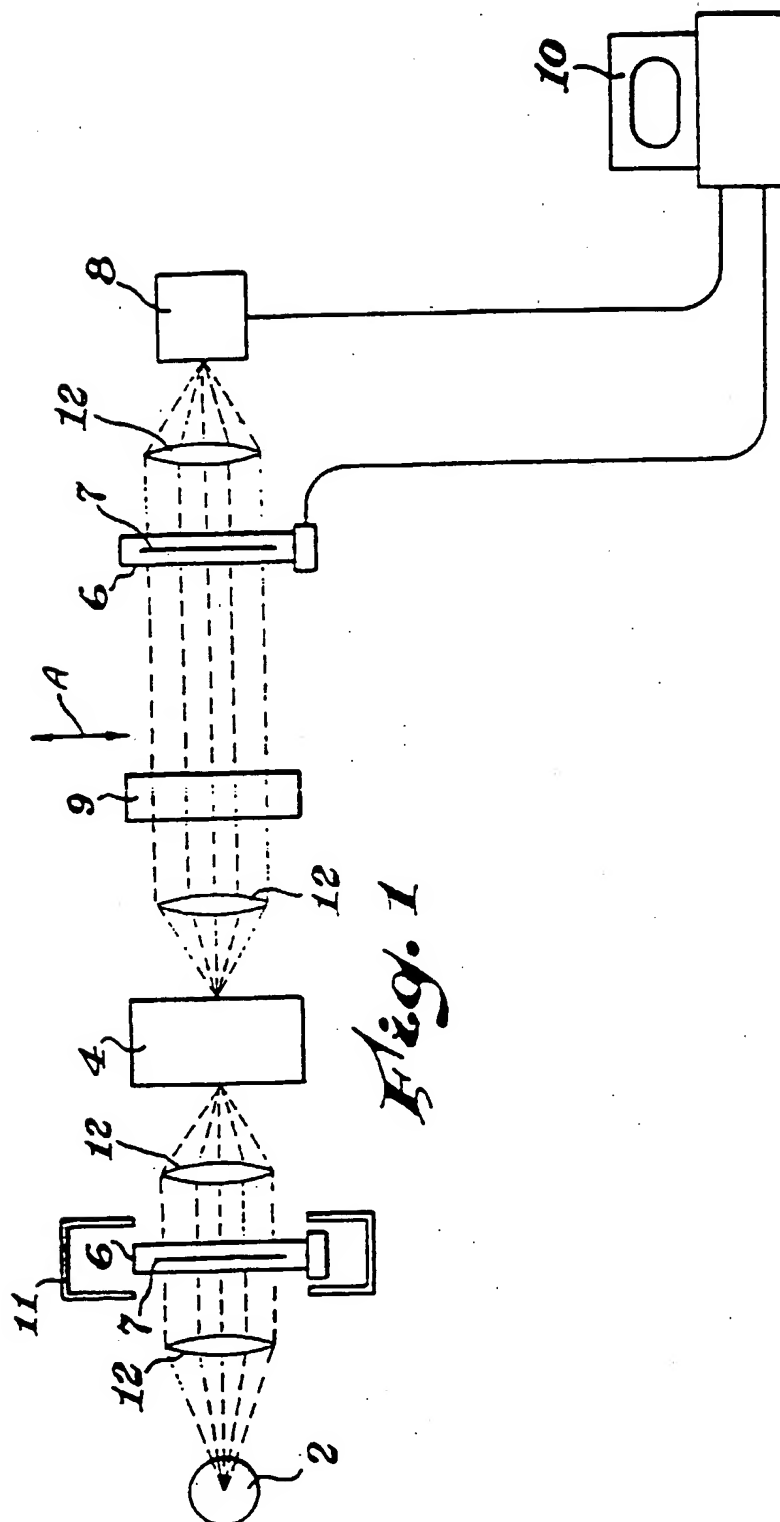


Fig. 1

FIGURE 2A

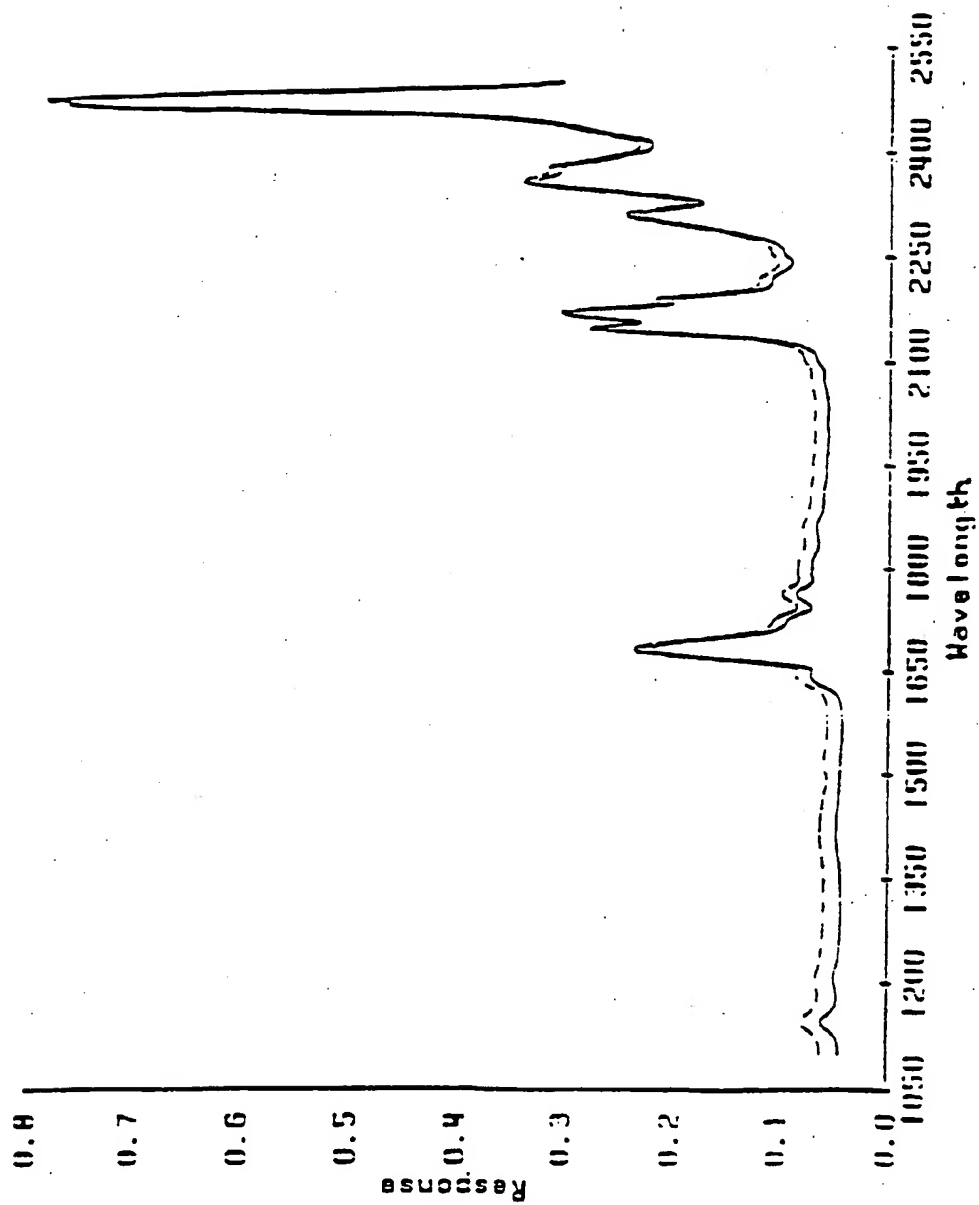


FIGURE 2B

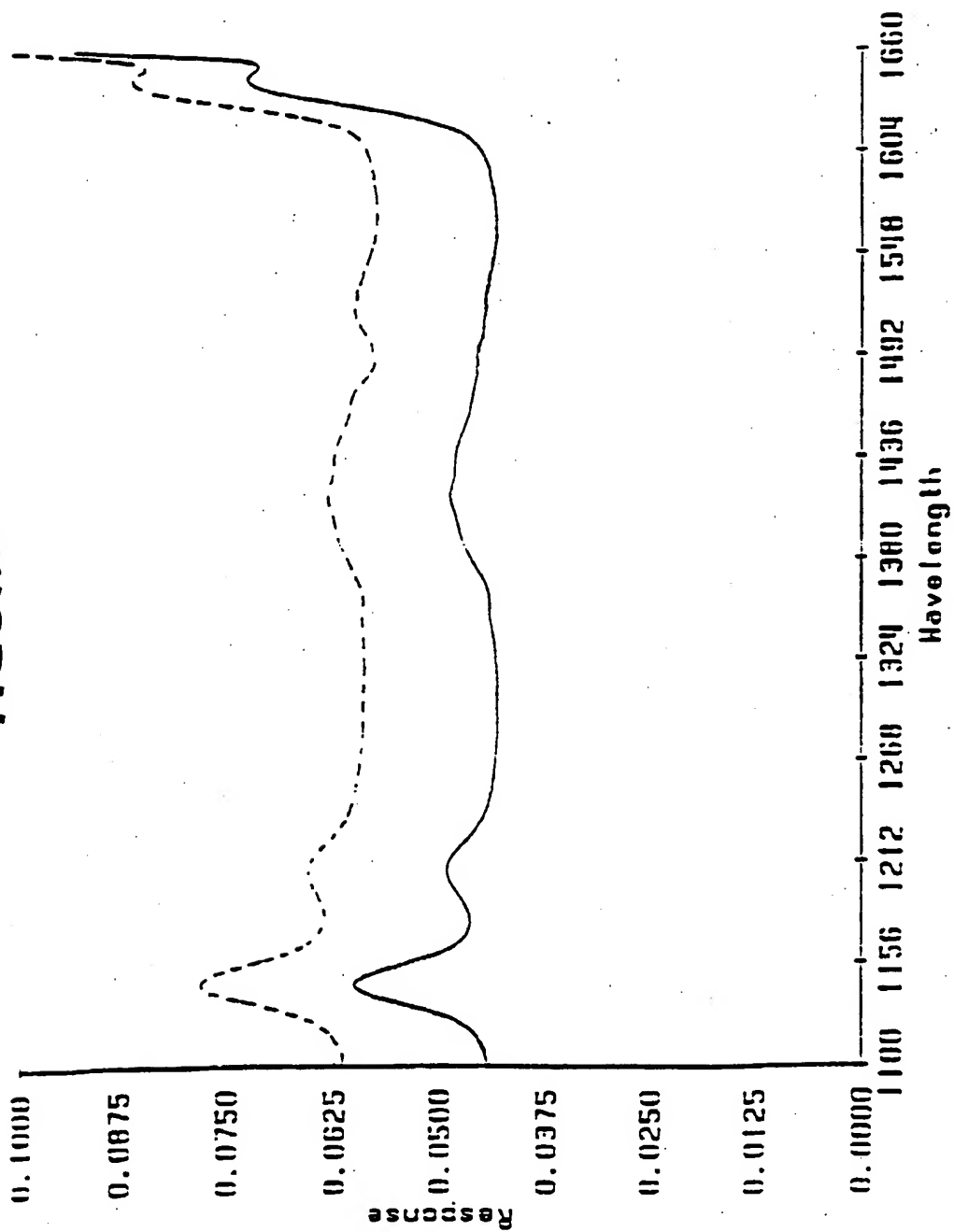


FIGURE 2C

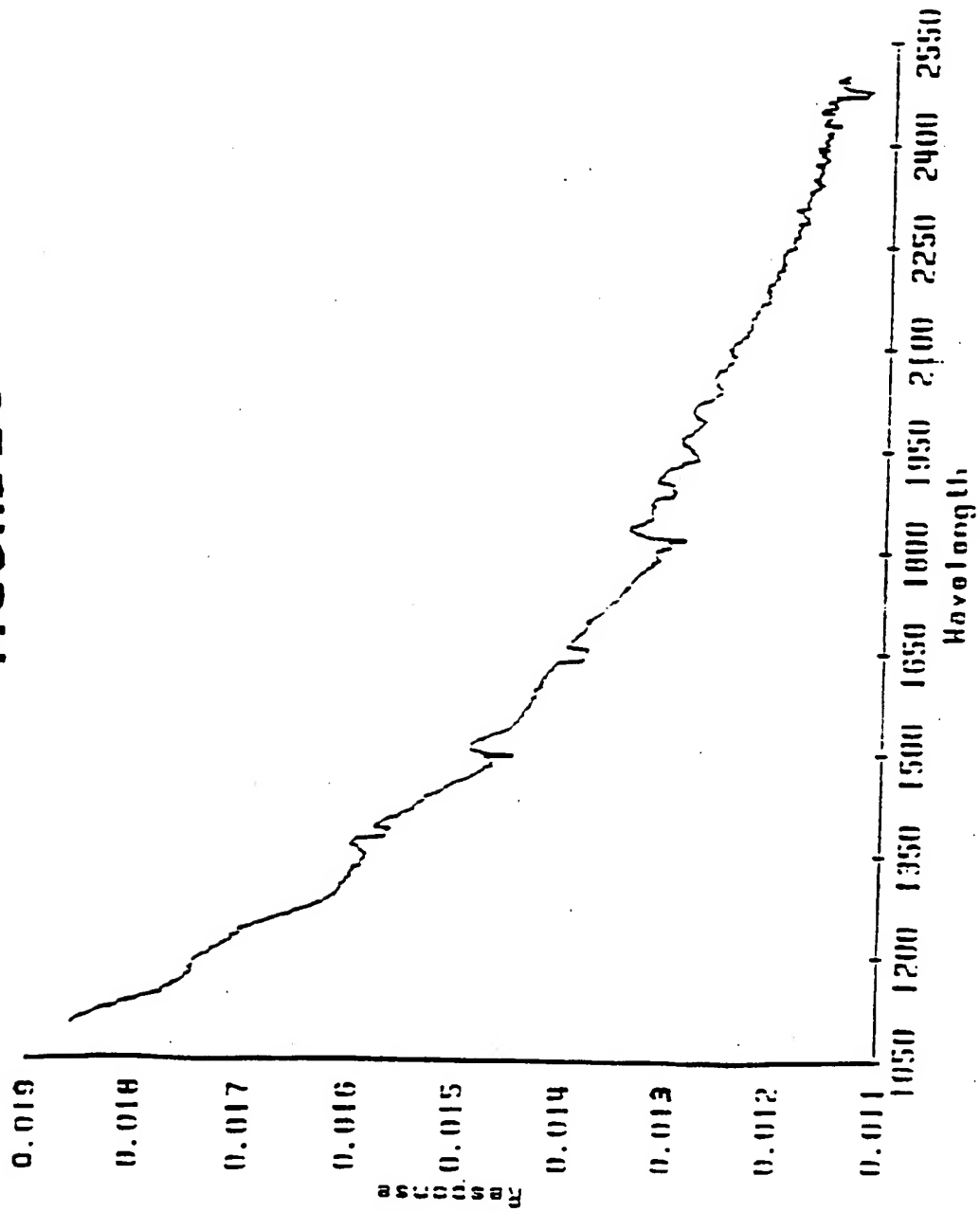
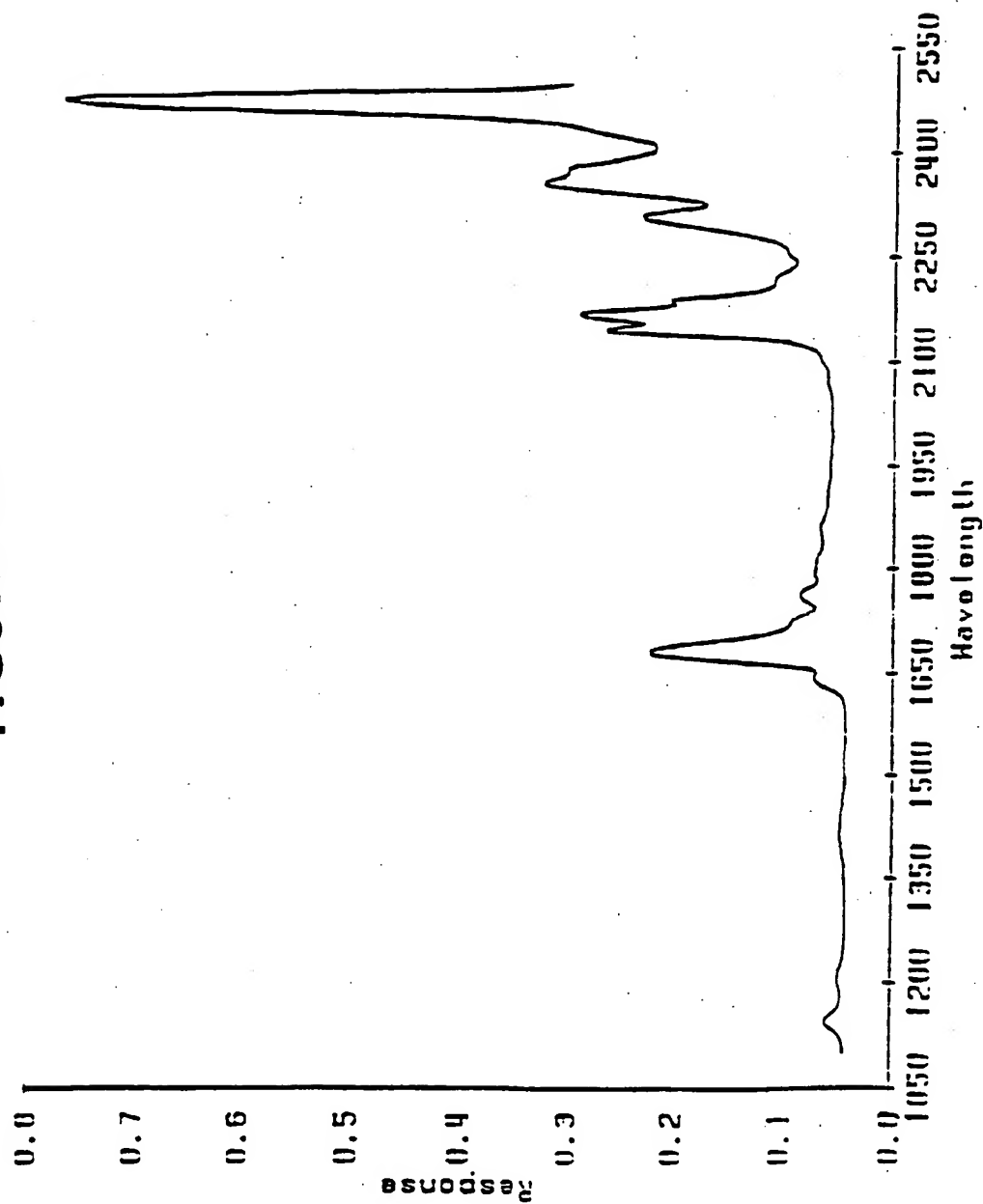


FIGURE 2D

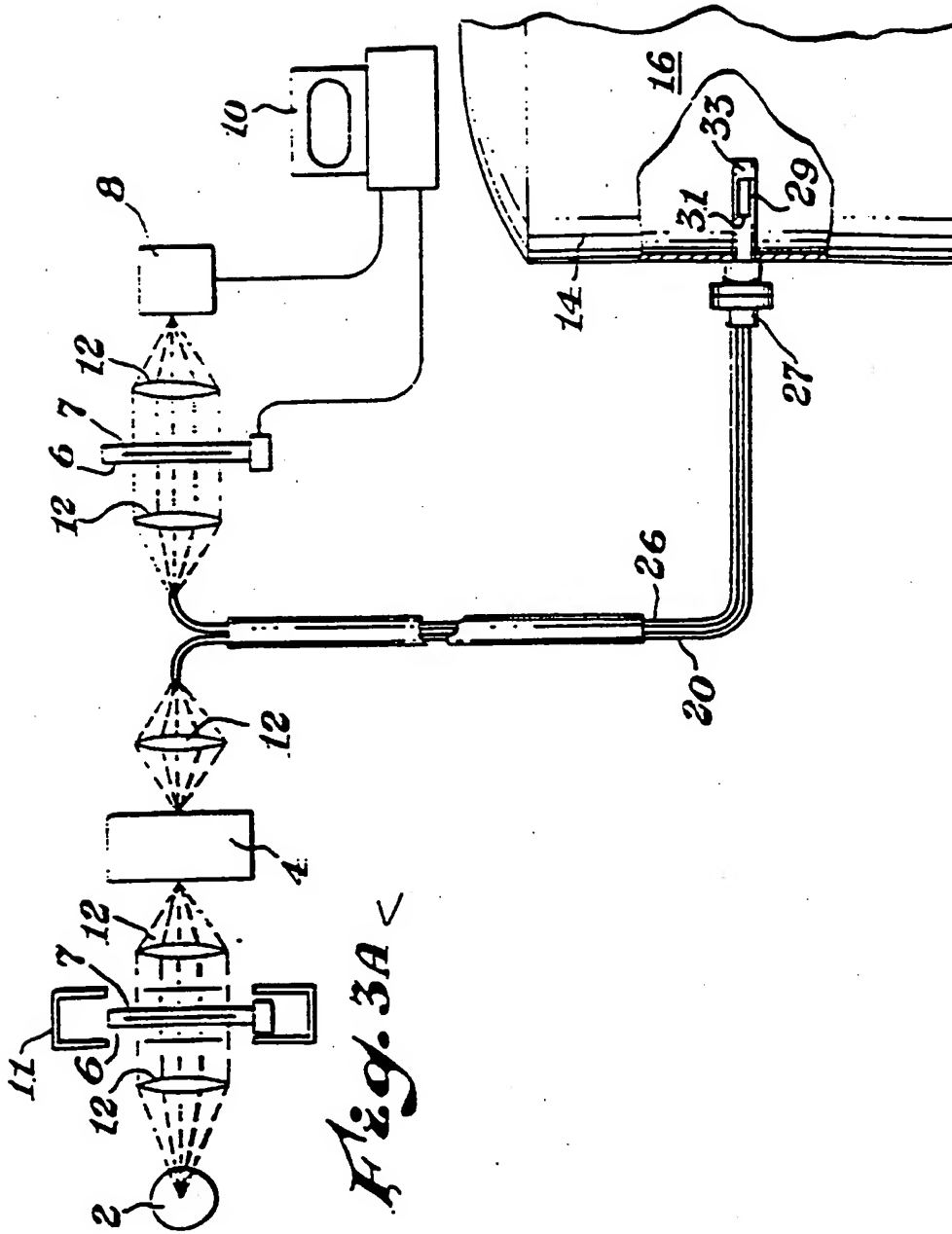


Fig. 3A

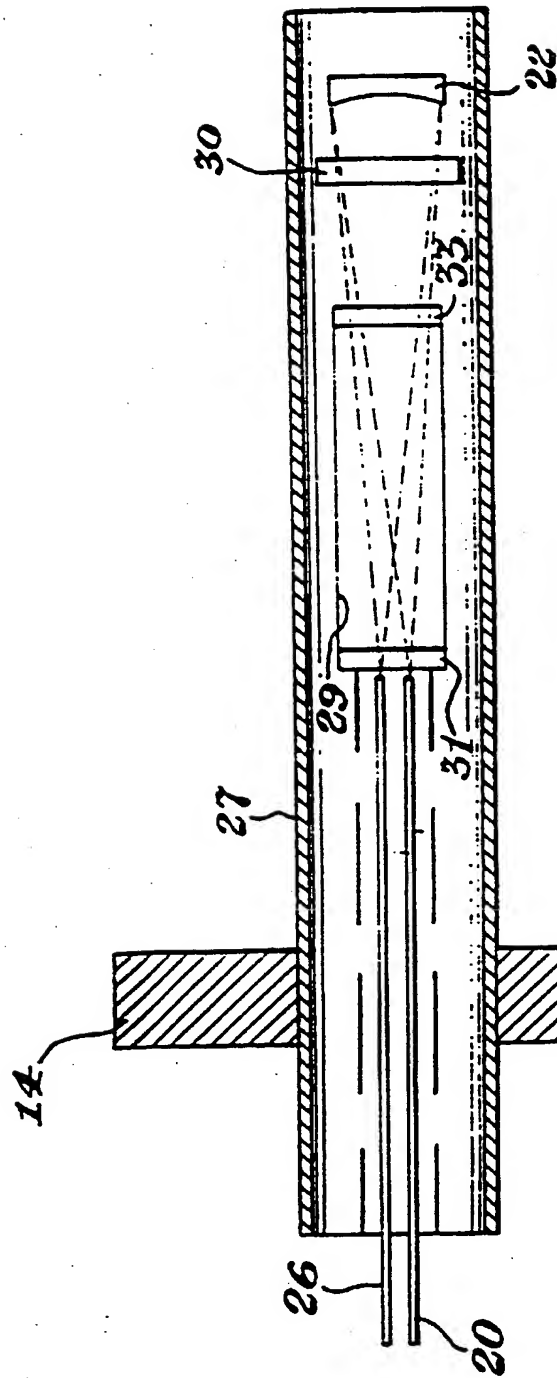


Fig. 3B

FIGURE 4A

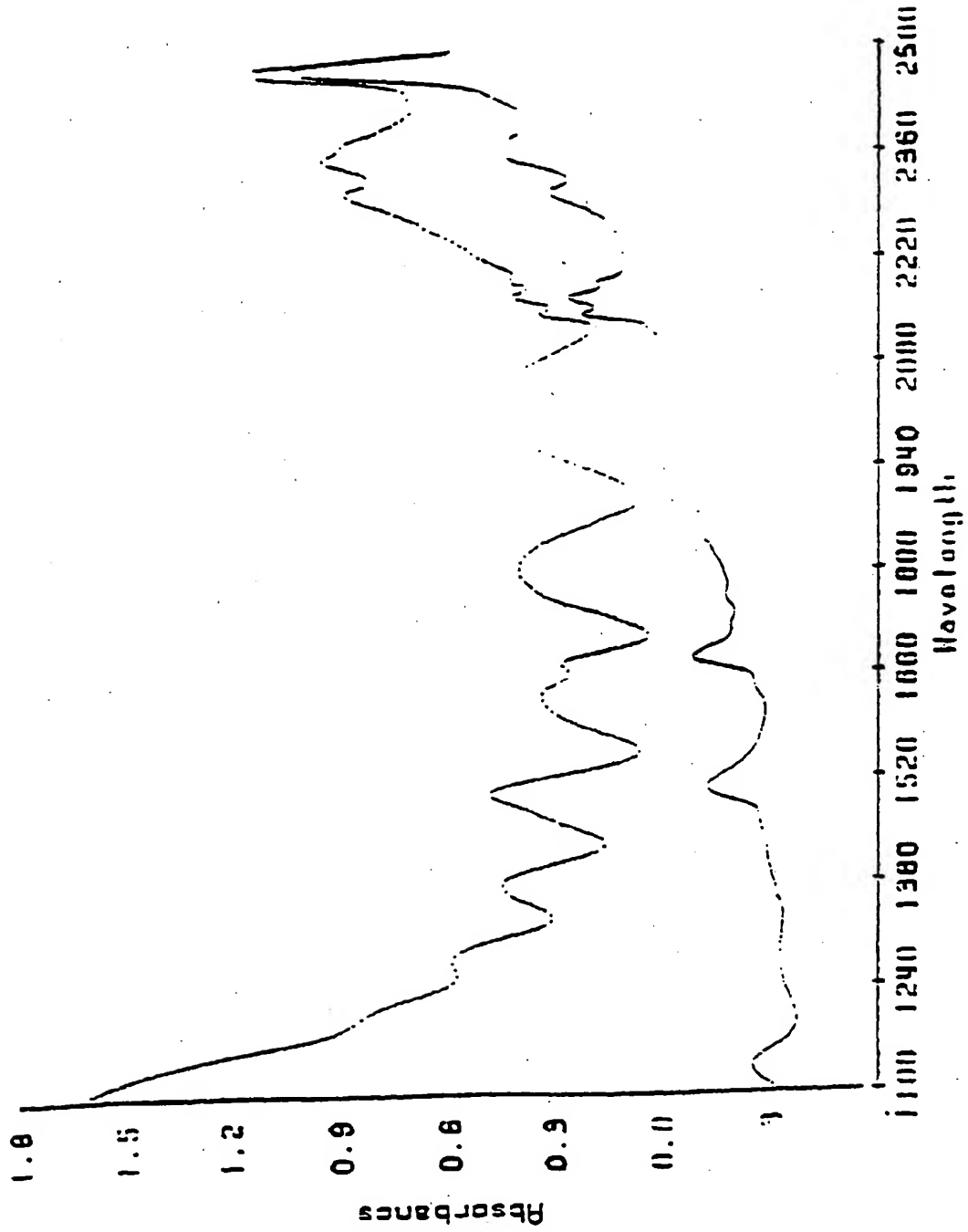


FIGURE 4B

Original Etalon Pattern Offset 0.3 nm

